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(54) Title: PECTINACEOUS GELLING AGENT

(57) Abstract

A pectinaceous gelling agent obtained from vegetable matter which contains pectinaceous substances having a degree of esterification of less than 50 %. The gelling agent contains 20 % to 50 % by weight of galacturonic acid and has a degree of esterification of 5 % to 20 %. The gelling agent may be prepared from waste vegetable matter by alkaline or acid extraction.

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Pectinaceous Gelling Agent

Field of the Invention

This invention relates to a pectinaceous gelling agent which has good gelling properties, to a process for its production, and to foodstuffs containing it.

Background to the Invention

Pectins are commonly used as gelling agents in foodstuffs. Gels are tri-dimensional networks formed by the gelling agent and that contain a liquid phase. Pectin gels are formed by hydrated pectins, after physical or chemical changes that decrease the solubility of the pectins. Pectins are found in nature in the middle lamella and primary cell walls of plant tissue. They are primarily straight-chained polymers of D-galacturonic acid in which the D-galacturonic acid units are linked by 1→4 glycosidic linkages. Neutral sugars such as galactose, glucose, rhamnose, arabinose and xylose may also be present; usually in the range of 5 to 10% by weight of the galacturonic acid. The rhamnose is often in the polymer as an interruption of the polygalacturonate sequences. The other sugars are usually found as side chains or as contaminating polysaccharides.

The functional group at the sixth carbon of each galacturonic acid unit may exist as a methyl ester or as a free carbonyl group. Two types of pectins are commonly distinguished on the basis of the extent of esterification of this functional group. One type is low methoxy pectins which have a degree of esterification (DE) of less than 50%; that is less than 50% of the total number of functional groups exist in the methyl ester form. The other type is high methoxy pectins which have a degree of esterification (DE) of greater than 50%.

This invention is concerned with low methoxy pectins. Low methoxy pectins form gels in the presence of alkaline earth metals; especially calcium. In the gels, the galacturonic acid units making up the polymer chain are cross-linked by divalent calcium ions. Gelation and the properties of the gel however depend upon many factors including pH, temperature, the degree of esterification, molecular weight, sugar content, calcium content and pectin content.

The main sources of commercial pectin products are citrus peels and apple pomace. Lemon and orange peels are one of the riches sources. However, many

vegetable materials which form wastes and by products contain pectin. Therefore there has been some interest in using these vegetable materials as commercial sources of pectin. For example, Sosulski, F *et al*; 1980; Przemysl Fermentacyjny i Owocowo-Warzywny, 24(3), 19-21 describe a process for the purification of pectin from sunflower stalks and flowers. The sunflower residue is extracted using an oxalate and polyphosphate solution and the pectins are precipitated from the extract using ethanol at a pH of 2. Pectin products which reportedly contain above 98% of galacturonic acids are obtained. The pectin products are reported in table 3 of Sosulski (*supra*) to have a degree of esterification of about 31 to 37%. This is said to be similar to pectin products obtained from citrus peel. However, all other factors being equal, the strength of gels made from low methoxy pectins increases as the degree of esterification decreases. Some workers have even reported hyperbolic relationships between the degree of esterification and breaking strength and gel sag (Kim, W.J. *et al*; 1978; J. Food Sci, 43, 572). Therefore the pectins obtained from the process described in Sosulski (*supra*) are unlikely to produce gels of sufficient strength in many applications; particularly where the gel is required to withstand retorting and sterilization processes.

Accordingly there is a need for pectinaceous gelling agents which have low degrees of esterification and which may be obtained from waste vegetable matter.

Summary of the invention

Accordingly, in one aspect, this invention provides a pectinaceous gelling agent obtained from vegetable matter containing pectinaceous substances that have a degree of esterification of less than about 50%, the gelling agent comprising about 20% to about 50% by weight of galacturonic acid and having a degree of esterification of about 5% to about 20%.

Surprisingly, it has been found that excellent gelling agents may be prepared from vegetable matter containing pectinaceous substances that have a degree of esterification of less than 50% by keeping the galacturonic acid content to below 50% by weight. Traditionally, efforts have been directed to obtaining extremely pure pectin products; for example with galacturonic acid contents above 80% by weight. However, these products contain pectinaceous substances which usually have a degree of esterification above about 30% and often above the degree of esterification of the pectinaceous substances in the vegetable matter

itself. However, the gelling agents of the invention contain pectinaceous substances having very low degrees of esterification; often half the degree of esterification of the pectinaceous substances in the vegetable matter itself.

The vegetable matter may be sunflower head and stalk residues. The pectin content of sunflower residues is about 22% by weight on a dry basis and the degree of esterification is about 15%. Preferably, when the vegetable matter is sunflower residue, the gelling agent contains about 35% to about 45% by weight of galacturonic acid and has a degree of esterification of about 5% to about 15%. Consequently gels produced using the gelling agents have excellent properties.

The vegetable matter may also be potato pulp, which is a waste material in the potato starch industry. The pectin content of potato pulp is about 15% by weight on a dry basis and the degree of esterification is about 17% to about 39%; generally about 30%. Preferably, when the vegetable matter is potato pulp, the gelling agent contains about 20% to about 30% by weight of galacturonic acid and has a degree of esterification of about 8% to about 18%.

In another aspect, this invention provides a process for the production of a pectinaceous gelling agent from vegetable matter that contains pectinaceous substances having a degree of esterification of less than about 50%, the process comprising:

subjecting comminuted vegetable matter to an acid or alkaline extraction in the presence of a sequestering agent for providing a pectinaceous extract;

separating the extract from the vegetable matter;

adjusting the pH of the extract to about 2 or less for causing a pectinaceous product to precipitate; and

neutralizing the precipitate to provide a pectinaceous gelling agent containing about 20% to about 50% by weight of galacturonic acid and having a degree of esterification of about 5% to about 20%.

For acid extraction, the comminuted vegetable matter may be suspended in an aqueous acid solution at a pH of about 3 to about 4.5. Preferably the solution is at a temperature of about 60 to about 85°C.

For alkaline extraction, the comminuted vegetable matter may be suspended in an aqueous alkaline solution at a pH of about 8 to about 12. Preferably the solution is at a temperature of about 5 to about 50°C.

Preferably the sequestering agent is a polyphosphate or citrate salt; for example sodium hexametaphosphate, tetrasodium pyrophosphate or sodium

citrate. Preferably about 0.1% to about 1% by weight of the sequestering agent is used.

The precipitate is preferably neutralized by suspending it in an aqueous solution at a pH of about 6 to about 7.5. Alcohol may then be added to the suspension for precipitating the pectinaceous gelling agent. The suspension may be a water suspension. The alcohol is preferably ethanol and the suspension preferably contains about 50% by weight of ethanol.

The invention also provides the gelling agent obtainable by the process defined above.

In another aspect, this invention provides a gelled emulsion product containing protein, lipid, carbohydrate and a binder, the binder comprising a gelling agent as defined above. Preferably the gelled emulsion product is a pet food.

Detailed description of the preferred embodiments

This invention provides a gelling agent which contains pectin. The gelling agent may be produced from waste vegetable matter which contains pectinaceous substances having a degree of esterification of less than 50%. Any suitable vegetable matter which is a source of low methoxy pectins may be used; for example the residues of sunflower heads and stalks, and potato pulp.

The vegetable matter is preferably comminuted prior to processing; for example by subjecting it to grinding or shredding. The comminuted vegetable matter may then be dried. To inactivate enzymes, the vegetable matter is preferably subjected to heat treatment. This may be accomplished by washing in hot water; for example at a temperature of about 70°C to about 90°C and for a time of about 10 to 30 minutes. Washing has the additional advantage of removing by-products.

The washed vegetable matter is then subjected to extraction; either under acid or alkaline conditions. Extraction may be carried out in any suitable manner. For example, the vegetable matter may be suspended in the appropriate solution in a stirred tank reactor. Alternatively, the extraction solution may be caused to flow through a fixed bed of the vegetable matter. Continuous extraction techniques may also be used.

For acid extraction, the extraction solution is an aqueous acid solution at a pH of about 3.0 to 4.5. The temperature is held at about 60 to 85°C. Any suitable acid may be used; for example hydrochloric acid.

For alkaline extraction, the extraction solution is an aqueous alkaline solution at a pH of about 8 to 12. The temperature is held at about 15 to 50°C; for example at room temperature. Any suitable alkaline may be used; for example sodium hydroxide.

A sequestering agent is preferably included in the acid or alkaline solution during extraction. The sequestering agent is conveniently a polyphosphate or citrate salt; preferably of a monovalent metal cation. Suitable examples sodium hexametaphosphate, tetrasodium pyrophosphate or sodium citrate. Typically, about 0.1% to about 1% by weight of the sequestering agent is used.

The extract is then separated off from the residual solid matter. This may be carried out by any suitable solid-liquid separation technique. Centrifugation is preferred. Pectinaceous matter is then caused to precipitate from the extract. This may be accomplished by adding an acid to the extract to lower the pH to about 2 or less. Any suitable alkaline may be used; for example sodium hydroxide. The precipitation is conveniently carried out at room temperature.

The precipitate is then separated from the liquid. Again any suitable solid-liquid separation technique may be used. Centrifugation is preferred. The precipitate is then neutralized to a pH of about 6 to about 7.5. This may be accomplished by suspending the precipitate in a neutral aqueous solution; for example water.

The precipitate may then be recovered, washed and dried to provide the gelling agent. Washing is preferably carried out with ethanol; for example in three stages using successively increasing concentrations. Concentrations of 70%, 80% and 95% are suitable. The drying may be carried out under vacuum at room temperature.

Alternatively, a suitable alcohol may be added to the neutral solution to cause the gelling agent to precipitate. Ethanol is a suitable alcohol. Typically, sufficient ethanol is added such that ethanol makes up at least about 50% by weight of the solution. If desired, sodium chloride may be added to the solution prior to the addition of the ethanol. The precipitate is then separated from the liquid. Again any suitable solid-liquid separation technique may be used. Centrifugation is preferred. The precipitate may then be washed and dried as before to provide the gelling agent.

The gelling agent obtained comprises about 20% to about 50% by weight of galacturonic acid; which is a relatively low concentration since most pectin-based gelling agents contain above 80% by weight of galacturonic acid. However the gelling agent has a degree of esterification of about 5% to about 20% which provides it with excellent gelling properties. Further the gelling agent is safe to use in food stuffs and hence may be used as a gelling agent for food stuffs. Suitable food stuffs include pet foods, gelled meat products, jellies, jams, and gelled dairy products. The gelling agent may also be used as a thickener or stabilizer in ice creams, juices and beverages.

However, due to the excellent gelling properties of the gelling agent, it is most suitably used in products which undergo retorting and sterilization; especially in the pet food industry. Examples of suitable products include gelled emulsion products such as gelled loaf products and gelled chunk-type products.

The gelled emulsion products typically contain protein, lipid, carbohydrate and a binder. The protein may be provided in the form of a meat material, animal or dairy proteins, and vegetable proteins, or mixtures of these proteins. Any suitable type of meat material may be used, for example, muscular or skeletal meat, meat by-products such as heart, liver, kidney, lung, or a mixture of meat and meat by-products. Further, the material may be obtained from any suitable source such as from livestock, poultry, and fish. Also, the meat material may be in the form of meat meals such as poultry meal, fish meal, red meat meal and mixtures thereof. Suitable animal or dairy proteins which may be used include egg proteins, gelatin, blood, and whey, or mixtures of these proteins. Suitable vegetable proteins which may be used include wheat gluten, soy flour, soy protein concentrates, soy protein isolates, pea protein isolates, etc, or mixtures of these proteins. The exact choice of protein used will depend upon factors such as availability, cost and palatability. Typically, the protein suitably comprises about 5 % to about 15% by weight of the gelled emulsion product.

The lipid may be provided in the form of suitable animal or vegetable fats and oils, or both. If the protein is provided in the form of a meat material, the meat material may well provide the desired amount of lipids and hence addition of further lipid may not be necessary. If it is necessary to add lipids, suitable examples of animal fats are tallow, chicken fats, pork fats, beef fats, and the like. Suitable examples of vegetable fats and oils are hydrogenated palm oil, corn oil, sunflower oil, rapeseed oil, and the like. Typically the emulsion product contains a maximum lipid level of about 25% by weight. Conveniently, the amount of

lipid in the emulsion is in the range of about 2% to 15% by weight; more preferably about 5% to about 12% by weight.

If it is necessary to add carbohydrate, the carbohydrate is preferably provided in the form of a starch or flour. Suitable carbohydrate sources are wheat starch, potato starch, corn starch, wheat flour, corn flour, oat flour, rye flour, rice flour, and the like. Sugars may also be added. Typically, for chunk products, the carbohydrate, in the form of starch or flour, comprises about 3% to about 15% by weight of the gelled emulsion product.

Additional ingredients such as salts, spices, seasonings, flavoring agents, minerals, and the like may also be included in the emulsion product. The amount of additional ingredients used is preferably such that they make up about 0.5% to about 5% by weight of the emulsion product.

The emulsion product may be prepared by emulsifying the protein, carbohydrates and lipids to provide a primary emulsion. The additional ingredients such as salts, spices, seasonings, flavoring agents, minerals, and the like may be added at this time. Water may also be included in the primary emulsion to provide from about 50% to about 90% by weight of the primary emulsion. If sufficient moisture is present in the protein, especially if the protein is provided as a meat material, water need not be added. A high speed emulsifier or homogeniser is particularly suitable for preparing the primary emulsion.

The gelling agent is then added to the primary emulsion; preferably in solution. Usually between about 0.5 % and about 5% by weight of the gelling agent is suitable. If necessary a calcium source is also added; for example calcium carbonate or calcium sulfate. Preferably calcium is present in an amount of about 40 to about 150 mg/g of gelling agent used. The primary emulsion is then subjected to further mixing or emulsification. The primary emulsion is then heated to a temperature above about 65°C; for example in a mixer-cooker. Steam may be injected into the primary emulsion if desired.

If it is desired to produce chunks, the heated emulsion may then be extruded, cooled and cut into chunks. The chunks may then be mixed with a suitable gravy or jelly and filled into cans or other containers. However, if it desired to produce a loaf type product, the heated emulsion may be filled directly into cans or other containers. The cans or other containers are then sealed and sterilized. Sterilization usually takes place at a temperature above about 120°C and for a period of at least about 15 minutes.

The gelled emulsion product obtained undergoes much less cook out of fats and starches giving a product with an excellent appearance. Further, the gelled emulsion product has a firm, relatively elastic texture.

The gelling agent may also be used to produce jelly type pet food products. These products may be produced by hydrating the gelling agent in water, with or without the presence of a buffer, and then adding a suitable calcium source. Meat chunks and the like may be added to the jelly.

Specific examples are now described for further illustration.

Example 1 - Extraction from Potato Pulp

A) Acid Extraction:- Wet potato pulp having a dry matter content of 20% to 30% by weight is used. The potato pulp is dried in an oven at 45°C and then ground to a size of 0.5 mm to 60 mesh. An amount of 500 g of the ground pulp is dispersed in 12.5 l of water at 85°C for 20 minutes. The water is removed using a centrifuge and the solid matter is suspended in 10 l of a solution at 75°C containing 0.5 % by weight of sodium hexametaphosphate. The pH is then adjusted to 3.5 using 5N HCl and the solution stirred for 1 hour. The extract is then recovered using a centrifuge.

The pH of the extract is adjusted to 2.0 using 32% HCl at 25°C. The extract is stirred for 10 minutes and the stored oyernight at 4°C. The precipitate which forms is recovered by centrifuging at 5000 rpm for 15 minutes. The precipitate is then suspended in 5 l of water and the solution neutralized using 32% NaOH to obtain a pH of about 6.5 to 7.0. An amount of 5 l of 95% ethanol is added to the solution to cause precipitation. The precipitate is recovered by centrifuging at 5000 rpm for 15 minutes. The precipitate is then washed three times; once with 70% ethanol, once with 80% ethanol and once with 95% ethanol. The washed precipitate is dried in a vacuum oven at room temperature to provide a gelling agent.

B) Alkaline extraction:- Wet potato pulp having a dry matter content of 20% to 30% by weight is used. The potato pulp is dried in an oven at 45°C and then ground to a size of 0.5 mm to 60 mesh. An amount of 500 g of the ground pulp is dispersed in 12.5 l of water at 85°C for 20 minutes. The water is removed using a centrifuge and the solid matter is suspended in 10 l of a 50 mM NaOH solution containing 0.75 % by weight of sodium hexametaphosphate. The pH is 12. The

solution stirred for 2 hours at room temperature. The extract is then recovered using a centrifuge.

The pH of the extract is adjusted to 2.0 using 6N HCl at 25°C. The extract is stirred for 10 minutes and the stored overnight at 4°C. The precipitate which forms is recovered by centrifuging at 5000 rpm for 15 minutes. The precipitate is then suspended in 5 l of water and the solution neutralized using 32% NaOH to obtain a pH of about 6.5 to 7.0. An amount of 5 l of 95% ethanol is added to the solution to cause precipitation. The precipitate is recovered by centrifuging at 5000 rpm for 15 minutes. The precipitate is then washed three times; once with 70% ethanol, once with 80% ethanol and once with 95% ethanol. The washed precipitate is dried in a vacuum oven at room temperature to provide a gelling agent.

Example 2 - Extraction from Sunflower Head Residues

A) Acid extraction:- The procedure of example 1A) is repeated but using sunflower head residues instead of potato pulp. The sunflower head residues contain 5% by weight of moisture.

B) Alkaline extraction:- The procedure of example 1A) is repeated but using sunflower head residues instead of potato pulp. The sunflower head residues contain 5% by weight of moisture.

Example 3 - Characterization of the gelling agents

Samples of the gelling agents of each of examples 1A, 1B, 2A and 2B are subjected to the following analysis:

- the Weibull-Stoldt method to determine fat content.
- the Kjeldahl method to determine protein content.
- hydrolysis of a 50 mg sample in 12N H_2SO_4 for 60 minutes at 30 °C and then in 0.4N H_2SO_4 for 75 minutes at 130°C. Monosaccharides are then determined using high performance anion exchange chromatography and pulsed amperometric detection.
- decarboxylation and measurement of the carbon dioxide produced to determine the galacturonic acid content.

- saponification and measurement by gas chromatography of the methanol release to determine the degree of methoxylation.

- drying in an oven for 4 hours at 104°C and the moisture content measured;

- roasting at 550°C for 12 hours and ash content then measured. The fat and protein contents of each gelling agent are determined from further samples using the Weibull-Stoldt and Kjeldahl methods respectively.

The results are as follows:

Characteristic	Example 1A	Example 1B	Example 2A	Example 2B
Moisture (%)	10.0 (3.0)	14.0 (3.0)	8.0 (6.0)	13.4 (6.0)
Extraction Yield (% on basis of dried pulp or residue)	29.0	20.0	11.0	11.0
Galacturonic acid (%)	40 (15.0)	25.8 (15.0)	38.6 (21.4)	38.0 (21.4)
Degree of esterification (%)	17.8 (22.8)	13.3 (22.8)	9.5 (15.3)	8.7 (15.3)
Rhamnose (%)	0.8 (0.8)	0.7 (0.8)	0.3 (0.7)	0.3 (0.7)
Arabinose (%)	3.4 (3.7)	2.3 (3.7)	0.3 (1.3)	0.4 (1.3)
Galactose (%)	12.4 (14.6)	10.3 (14.6)	0.3 (1.7)	0.3 (1.7)
Glucose (%)	9.5 (51.4)	19.1 (51.4)	0.5 (18.6)	0.7 (18.6)
Xylose (%)	-	-	0.1 (5.6)	0.1 (5.6)
Ashes (%)	21.0 (3.8)	23.9 (3.8)	38.2 (16.6)	38.2 (16.6)
Fat (%)	0.2 (0.2)	0.2 (0.2)	2.0 (2.3)	2.0 (2.3)
Protein (%)	2.5 (5.3)	3.0 (5.3)	6.0 (7.8)	6.0 (7.8)

Values in parenthesis are those for the starting vegetable material.

Example 4 - Gel preparation and rheological measurements

A sample of a gelling agent of each of examples 1B, 2A and 2B is separately dispersed in water. For the gelling agent of example 2A, a citrate buffer is included in the water. In the case of the gelling agent of example 1B, the pH is 6.4, for the gelling agent of example 2A, the pH is 6.5, and for the gelling

agent of example 2B, the pH is 7.1. In each case, the suspension is held at a selected hydration temperature for about 2 hours. A selected amount of a solution containing 2.9 % by weight of $CaSO_4.2H_2O$ is then added to obtain a desired calcium concentration. The concentration of the gelling agent is 2% by weight. The solution is then stirred for about 1 minute, poured into a mold, and stored at 4°C for 24 hours. The gelled products are then removed and subjected to analysis. In all cases, the gelling agent provides 2% by weight of the gel.

The elastic modulus E, which is a measure of gel firmness, is determined for each gelled product using a Micro System TA-XT2 Texture Analyzer. The strain applied during the measurement is 10% and the plate speed is 0.8 mm/s.

The process is repeated for the gelling agents of examples 1B and 2B but including sodium citrate during hydration.

The results are as follows:

Sample	Hydration Temperature (°C)	Ca^{2+} Concentration (mg/g extracted product)	Sodium citrate Concentration (mM)	Elastic Modulus (Pa)
1B	25	40	-	42000
	25	40	8	15000
	25	100	8	24000
	60	40	8	150000
2A	25	40	8	48000
	25	40	10	12000
	60	40	8	64000
	80	40	8	70000
	25	100	8	57000
2B	25	40	8	80000
	60	40	8	135000
	25	100	8	260000

The results indicate that increasing the presence of sodium citrate decreases the elastic modulus of all gelled products. Further, the results indicate that increasing the amount of calcium present in general increases the elastic modulus of all gelled products.

For the gelling agents of example 1B and 2B, a maximum elastic modulus is reached at a hydration temperature of about 60°C. However, for the gelling agent of example 1B, the elastic modulus increases steadily at hydration temperatures above about 40°C, and For the gelling agent of example 1B, the maximum is reached at a hydration temperature of about 60°C.

The elastic modulus of the gelled products produced using the gelling agent of example 2A is affected by the pH of the hydration solution. A maximum elastic modulus is obtained with a pH of about 6.0 to 6.7.

These results indicate that the gel firmness may be readily adjusted by varying parameters such as calcium content, pH, hydration temperature, sodium citrate presence, etc, to achieve a desired level.

Example 5 - Production of pet food chunks

Frozen beef is comminuted and emulsified with beef fat in a homogenizer. Carbohydrate, in the form of wheat starch, and salt are added and the mixture mixed at low speed. Water containing $CaSO_4.2H_2O$ is added and the mixture emulsified at high speed.

The mixture is divided into three parts. A sample of a gelling agent of examples 1B, 2A and 2B is added to a separate mixture. The mixtures are heated treated at 78°C for 30 minutes and then allowed to cool to form gelled emulsion products. The gelled emulsion products are cut into chunks and filled into cans with water. The cans are sealed and sterilized at 121°C for 20 minutes. The cans are then allowed to cool.

The cans are opened and the contents visually inspected. The chunks are well-formed and little or no cook out of fat or starch is noticeable. Further the chunks retain their shape and have a firm texture.

Example 6 - Production of a pet food loaf

Frozen liver, lungs, and kidneys are comminuted and mixed at low speed with water and salts, including $CaSO_4.2H_2O$. The mixture is then emulsified at high speed, heated to 35°C and divided into two parts. A gelling agent of each of examples 2A and 2 B is added to water and hydrated at 70°C for 15 minutes. Each gelling agent solution is then added to a separate emulsion. The mixtures are then filled into cans, the cans are sealed and retorted at 121°C for 20 minutes.

The cans are opened and the contents visually inspected. In both cases, the meat matrix is gellified, retains its shape and has a firm texture.

Claims

1. A pectinaceous gelling agent obtained from vegetable matter containing pectinaceous substances having a degree of esterification of less than 50%, the gelling agent comprising 20% to 50% by weight of galacturonic acid and having a degree of esterification of 5% to 20%.

2. A gelling agent according to claim 1 in which the vegetable matter is sunflower head residues and the gelling agent contains 35% to 45% by weight of galacturonic acid and has a degree of esterification of 5% to 15%.

3. A gelling agent according to claim 1 in which the vegetable matter is potato pulp and the gelling agent contains 20% to 30% by weight of galacturonic acid and has a degree of esterification of 8% to 18%.

4. A gelled emulsion product containing protein, lipid, carbohydrate and a binder, the binder comprising a gelling agent according to claim 1.

5. A process for the production of a pectinaceous gelling agent from vegetable matter containing pectinaceous substances having a degree of esterification of less than 50%, the process comprising:

subjecting comminuted vegetable matter to an acid or alkaline extraction in the presence of a sequestering agent for providing a pectinaceous extract;

separating the extract from the vegetable matter;

adjusting the pH of the extract to about 2 or less for causing a pectinaceous product to precipitate; and

neutralizing the precipitate to provide a pectinaceous gelling agent containing about 20% to about 50% by weight of galacturonic acid and having a degree of esterification of about 5% to about 20%.

6. A process according to claim 5 in which the comminuted vegetable matter is extracted by suspending it an aqueous acid solution at a pH of 3 to 4.5 in the presence of 0.2 to 1% by weight of a sequestering agent and at a temperature of 60 to 85°C.

7. A process according to claim 5 in which the comminuted vegetable matter is extracted by suspending it in an aqueous alkaline solution at a pH of 8 to 12 in the presence of 0.2 to 1% by weight of a sequestering agent and at a temperature of 5 to 50°C.

8. A process according to claim 6 or claim 7 in which the sequestering agent is a polyphosphate or citrate salt of a monovalent metal ion.

9. A process according to claim 5 in which the precipitate is neutralized in a suspension at a pH of 6 to 7.5 and alcohol is added to the suspension for precipitating the pectinaceous gelling agent.

10. A pectinaceous gelling agent obtained from vegetable matter containing pectinaceous substances having a degree of esterification of less than 50%, the gelling agent comprising 20% to 50% by weight of galacturonic acid and having a degree of esterification of 5% to 20% and obtainable by a process comprising:

subjecting comminuted vegetable matter to an acid or alkaline extraction in the presence of a sequestering agent for providing a pectinaceous extract;

separating the extract from the vegetable matter;

adjusting the pH of the extract to about 2 or less for causing a pectinaceous product to precipitate; and

neutralizing the precipitate to provide the pectinaceous gelling agent.

INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/EP 97/03289

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A23L1/0524 C08B37/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A23L C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	FR 2 287 180 A (MARS LIMITED) 7 May 1976 see page 2, line 35 - page 3, line 18 see page 11, line 14 - line 31 see page 12, line 8 - line 12 see claim 1	1-4
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X	F.SOSULSKI ET AL.: "Sunflowers as raw material for production of low-methylated pectin" PRZEMYSL FERMENTACYJNY I OWOCOWO-WARZYWNY, vol. 24, no. 3, 1980, WARSZAWA, POLAND, pages 19-21, XP000196654 cited in the application see abstract; figure 1; table 3	1-3,5,6, 8,10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 September 1997	22.10.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,	Alvarez Alvarez C

INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/EP 97/03289

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	K.C.CHANG ET AL.: "Sunflower head residue pectin extraction as affected by physical conditions" JOURNAL OF FOOD SCIENCE, vol. 59, no. 6, 1994, pages 1207-1210, XP000612309 see the whole document	1-3,5,6, 8-10
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 262 (C-608), 16 June 1989 & JP 01 065101 A (TAKESHI ISHII ET AL.), 10 March 1989, see abstract	5,7
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A	W.J.KIM ET AL.: "Effect of chemical composition on compressive mechanical properties of low ester pectin gels" JOURNAL OF FOOD SCIENCE, vol. 43, no. 2, March 1978, pages 572-575, XP002041982 cited in the application	

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